

## CLAIMS

I claim:

1. A process for treatment of an aqueous feed stream in heat transfer equipment, said heat transfer equipment comprising at least one evaporator with at least one heat transfer surface, to produce a low solute containing distillate stream and a high solute/solids containing blowdown stream, in which said feed stream has  
5 minimal tendency to scale said heat transfer surface, said process comprising:

(a) providing a feed water stream containing soluble and insoluble inorganic and organic species therein, said species comprising:

(II) multi-valent metal cations,

(III) alkalinity,

10 (IV) at least one molecular species which is at low ionization levels when in solution at around neutral pH;

(b) removing a portion or substantially all multi-valent cations metal from said feed stream, and

15 (c) reducing the tendency of said feed water or form scale on said heat transfer surfaces, when said feed water is concentrated to a selected concentration factor at a selected pH, by effecting, in any order, one or more of the following;

(I) removing substantially all alkalinity from said feed water stream;

20 (II) removing dissolved gas from said feed water stream;

(III) raising the pH of said feed water stream to at least about 9 or higher;

(d) passing the product from step (c) into said heat transfer equipment, wherein said heat transfer equipment:

25 (I) contains a plurality of heat transfer surfaces,

(II) contains a circulating high solids solution, and

(III) wherein the pH of said circulating solution is maintained to at least about 9, or higher,

(e) so as to concentrate said feed water to said selected concentration factor, to produce:

- (I) a high solute/solids containing blowdown stream, and
- (II) a low solute containing distillate stream.

2. The process as set forth in claim 1, wherein the step of removing said multi-valent cations includes removing substantially all said alkalinity associated with hardness, and is accomplished in a single unit operation.

3. The process as set forth in claim 2, wherein said single unit operation comprises a weak acid cation ion exchange system operated in a hydrogen form.

4. The process as set forth in claim 1(b), wherein the step of said multi-valent cation removal is accomplished in a weak acid cation ion exchange system that is operated in a sodium form.

5. The process as set forth in claim 1, further comprising the step of adding acid before the step of removing said dissolved gas, to effect conversion of alkalinity to carbon dioxide.

6. The process as set forth in claim 3, wherein said feed water stream contains more multi-valent cations than alkalinity, and further comprising, before feeding said feed water to said weak acid cation exchange system, the step of adjusting the ratio of multi-valent cations to alkalinity by adding a base to said feed water, so as to raise the alkalinity of said feed water.

7. The process as set forth in claim 3, wherein said feed water stream contains more alkalinity than multi-valent cations, and further comprising, before feeding said feed water to said weak acid cation exchange system, the step of addition of acid to said feed water, so as to remove the excess alkalinity in said feed water.

8. The process as set forth in claim 1, wherein the step of multi-valent cation removal is accomplished by passing said feed water through a sodium form strong acid cation ion exchange system.

9. The process as set forth in claim 1, wherein in step (c), the pH is raised to between 10 and 11.

10. The process as set forth in claim 1, wherein in step (c), the pH is raised to between 9 and 10.

11. The process as set forth in claim 10, wherein said sparingly ionized species when in neutral or near neutral pH aqueous solution comprises a weak acid with a  $pK_{a1}$  of about 7.5 or higher.

12. The process as set forth in claim 1, wherein in step (c), the pH is raised to between 11 and 12.

13. The process as set forth in claim 1, wherein in step (c), the pH is raised to between 12 and 13.

14. The process as set forth in claim 1, wherein in step (c), the pH is raised to greater than or at least about 13.

15. The process as set forth in claim 1, wherein said low ionized species when in neutral or near neutral pH aqueous feed stream comprises silica ( $\text{SiO}_2$ ).

16. The process as set forth in claim 1, wherein said low ionized species when in neutral or near neutral pH aqueous feed stream comprises meta/ortho silicic acid ( $\text{H}_4\text{SiO}_4$ ).

17. The process as set forth in claim 1, wherein said low ionized species when in neutral or near neutral pH aqueous feed stream comprises an ionizable organic carbon species.

18. The process as set forth in claim 1, wherein said low ionized species when in neutral or near neutral pH aqueous feed stream comprises boron, or derivatives thereof.

19. The process according to claim 1, wherein the step of removal of multi-valent cations is accomplished by addition of an alkali to simultaneously raise pH while precipitating hardness from said feed water stream.

20. The process as set forth in claim 1, further comprising the step of adding caustic before the step of removing dissolved gas, to effect removal of gasses such as ammonia.

21. The process as set forth in claim 1, wherein said at least one molecular species which is at low ionization levels when in solution at around neutral pH comprises silica, and wherein said blowdown stream contains silica up to about 160 ppm.

22. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 2500 ppm.

23. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 5000 ppm.

24. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 7500 ppm.

25. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 10,000 ppm.

26. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 20,000 ppm.

27. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 50,000 ppm.

28. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 75,000 ppm.

29. The process as set forth in claim 21, wherein said silica is present in said blowdown stream at up to about 100,000 ppm.

30. The process as set forth in claim 1, wherein said feed water stream comprises silica, and wherein said heat transfer equipment is operated without limitation of the concentration of silica present in said blowdown stream.

31. The process according to claim 1, wherein the ratio of the quantity of said distillate stream produced to the quantity of said feed water stream provided is greater than about 50%.

32. The process according to claim 1, wherein the ratio of the quantity of said distillate stream produced to the quantity of said feed water stream provided is greater than about 85%.

33. The process according to claim 1, wherein the ratio of the quantity of said distillate stream produced to the quantity of said feed water stream provided is greater than about 95%.

34. The process according to claim 1, wherein the ratio of the quantity of said distillate stream produced to the quantity of said feed water stream provided is greater than about 99%.

35. The process according to claim 1, wherein said heat transfer equipment comprises falling thin film evaporation equipment, operating as a single unit, or operating in series, or operating in parallel to generate said distillate stream and said blowdown stream.

36. The process according to claim 1, wherein said heat transfer equipment comprises forced circulation evaporation equipment operating as a single unit or operating in parallel to generate said distillate stream and a high solids blowdown stream.

37. The process according to claim 1, wherein said heat transfer equipment comprises natural circulation evaporation equipment operating as a single unit or operating in parallel to generate said distillate stream and a high solids blowdown stream.

38. The process according to claim 35 or claim 36 or claim 37, wherein said heat transfer surfaces are tubular.

39. The process according to claim 35 or claim 36 or claim 37, wherein said heat transfer surfaces are plates.

40. The process as set forth in claim 38 or claim 39, wherein said heat transfer surfaces are operated in a vertical position.

41. The process as set forth in claim 38, wherein said heat transfer surfaces are operated in a horizontal position.

42. The process as set forth in claim 38 wherein said heat transfer surfaces are designed for enhanced heat transfer.

43. The process as set forth in claim 38 wherein said circulating solution is heated on the interior of the tubes.

44. The process as set forth in claim 38 or claim 39, wherein said circulating solution is heated on the exterior of the tubes or plates.

45. The process as set forth in claim 39, wherein said plates are die pressed plates.

46. The process as set forth in claim 39, wherein said plates are made from flat sheets welded together and then formed into final shape by internal pressure.

47. The process as set forth in claim 39, wherein said plates are fabricated as welded assemblies.

48. The process as set forth in claim 39, wherein said plates are gasketed.

49. The process as set forth in claim 35 or claim 36 or claim 37, wherein said heat transfer equipment is operated in a steam driven multiple effect mode.

50. The process as set forth in claim 35 or claim 36 or claim 37, wherein said heat transfer equipment is operated in a mechanical vapor recompression mode.

51. The process as set forth in claim 35 or claim 36 or claim 37, wherein said heat transfer equipment is operated in a thermal compression mode.

52. The process as set forth in claim 35 or claim 36 or claim 37, wherein said heat transfer equipment is operated as a multiple stage flash evaporator.

53. The process as set forth in claim 35 or claim 36 or claim 37, further comprising the step of treating said high solute concentrate stream in a crystallizer operating as a single unit or operating in parallel to generate said distillate stream and said high solids blowdown stream.

54. The process as set forth in claim 36 or claim 53, comprising the step of further treating said high solids blowdown stream after reaching said selected concentration factor in a solids dewatering device operating as a single unit or operating in parallel.

55. The process as set forth in claim 54, further comprising the step of generation of a high solute low suspended solids filtrate water stream, and still further comprising the step of directing said low filtrate water stream to the inlet of said heat transfer equipment for further processing.

56. The process as set forth in claim 55, further comprising the step of generation of a dry solids product for disposal.

57. The process as set forth in claim 1, wherein the step of removing said dissolved gases, is further comprised of lowering the pH of said feed stream to remove any remaining alkalinity and release carbon dioxide.

58. The process as set forth in claim 57, further comprised of heating said acidified feed water stream to enhance gas removal in a degasifier prior to entering said heat transfer equipment.

59. The process as set forth in claim 1, wherein step (d) further comprising distributing said circulating solution across one side of said plurality of heat transfer surfaces to generate a steam vapor.

60. The process as set forth in claim 59, further comprising collecting said steam vapor and slightly compressing it to form a compressed steam vapor.

61. The process as set forth in claim 60, further comprising directing said compressed steam vapor to a second side of said plurality of heat transfer surfaces to condense said compressed steam vapor into said distillate stream.

62. The process according to claim 1, wherein the step of raising the pH is accomplished by addition of a base in aqueous solution, said base selected from the group consisting of (a) sodium hydroxide, (b) sodium carbonate, (c) potassium hydroxide, and (d) potassium carbonate.

63. The process according to claim 1, wherein the step of raising the pH is accomplished by addition of an aqueous organic base.

64. The process according to claim 1, wherein the ratio of the quantity of said distillate stream produced to the quantity of said feed water stream provided is between 90 and 98 percent.

65. The process according to claim 1, wherein said feed water stream further comprises cooling tower blowdown.

66. The process according to claim 1, wherein said feed water further comprises scrubber blowdown.

67. The process according to claim 1, wherein said feed water further comprises water utilized in ash transport in a coal fired steam-electric power plant.

68. The process according to claim 1, wherein said feed water stream comprises ash pond water.

69. The process according to claim 1, wherein said feed water stream comprises ash-sluicing water.

70. The process according to claim 1, wherein said feed water stream comprises effluent from sewage treatment.

71. The process according to claim 1, wherein said feed water stream comprises effluent from a food processing treatment.

72. The process according to claim 1, wherein said feed water stream comprises boiler blowdown.

73. The process according to claim 1, wherein said feed water stream comprises a concentrated stream from membrane separation equipment.

74. The process according to claim 1, wherein said feed water stream comprises effluent from oil refining operations.

75. The process as set forth in claim 35 or claim 36 or claim 37, comprising the step of further treating said high solids blowdown stream after reaching said selected concentration factor in a spray dryer to dry solids.



76. The process as set forth in claim 1, wherein the step of multi-valent cation removal is partially accomplished by passing said feed water stream through membrane softening equipment.

77. The process as set forth in claim 1, wherein the step of multi-valent cation removal is accomplished by increasing the pH to at least about 10 in said feed water stream and passing the pH adjusted stream through membrane separation equipment to filter out hardness precipitate.

78. In a process for the concentration of an aqueous feed stream in an evaporator to produce a low solute containing distillate stream, and retaining at least a portion of said aqueous feed stream in said evaporator to increase the concentration of a solute to a selected concentration factor at a selected pH in said retained portion of said aqueous feed stream, the improvement which comprises feeding said evaporator with an aqueous feed stream characterized at the time of initial entry into said evaporator, by:

- (I) substantially no multi-valent cations,
- (II) substantially no alkalinity,
- (III) substantially no dissolved or suspended gases, and
- (IV) a pH of at least 9 or above.

79. The process as set forth in claim 78 wherein greater than 80% of the multi-valent cations are removed from said feed stream.

80. The process as set forth in claim 78 wherein greater than 90% of the multi-valent cations are removed from said feed stream.

81. The process as set forth in claim 78 wherein greater than 98% of the multi-valent cations are removed from said feed stream.

82. The process as set forth in claim 78 wherein greater than 80% of the alkalinity is removed from said feed stream.

83. The process as set forth in claim 78 wherein greater than 90% of the alkalinity is removed from said feed stream.

84. The process as set forth in claim 78 wherein greater than 98% of the alkalinity is removed from said feed stream.

85. The process as set forth in claim 78 wherein greater than 80% of the gases are removed from said feed stream.

86. The process as set forth in claim 78 wherein greater than 90% of the gases are removed from said feed stream.

87. The process as set forth in claim 78 wherein greater than 98% of the gases are removed from said feed stream.

88. The process as set forth in claim 78 wherein said bases are selected from the group consisting of carbon dioxide, ammonia, oxygen, nitrogen and mixtures thereof.

89. The process as set forth in claim 78, wherein said aqueous feed stream is further characterized by minimizing or eliminating scale inhibitor solution or scale dispersant solution in said aqueous feed stream.

90. A method for treating a feed water stream, in a least one evaporator system and for simultaneously (a) reducing the scaling potential and (b) allowing an increased heat transfer rate and (c) allowing higher recovery and (d) minimizing or eliminating scale control methods in an existing heat transfer system, to produce a  
5 low solute containing distillate stream and a high solute/solids containing blowdown stream, said method comprising:

(a) providing a feed water stream containing soluble and insoluble species therein, said species comprising two or more of the following:

(I) multi-valent metal cations,

10 (II) alkalinity, and

(III) at least one molecular species which is at low ionization levels when in solution at around neutral pH;

(b) removing a portion or substantially all multi-valent cations from said feed stream, and

- 15 (c) reducing the tendency of said feed water to form scale when  
said feed water is concentrated to a selected concentration factor at a selected  
pH, by effecting, in any order, one or more of the following;
- (I) removing substantially all alkalinity from said feed water  
stream;
- 20 (II) removing dissolved or suspended gases from said feed  
water stream, whether initially present or created during said multi-  
valent cation or said alkalinity removal step or said pH adjustment  
step;
- (III) raising the pH of said feed water stream to at least about 9  
25 or higher;
- (d) passing the product from step (c) into heat transfer equipment,  
wherein said heat transfer equipment:
- (I) contains a plurality of heat transfer surfaces,  
(II) contains a circulating high solutes/solids solution, and  
30 (III) the pH of said circulating solution is maintained to at least  
about 9, or higher,
- (e) so as to concentrate said feed water to said selected  
concentration factor, to produce:
- (I) a high solute/solids containing blowdown stream, and  
35 (II) a low solute containing distillate stream.

91. In a process for the purification of an aqueous feed stream comprising  
solutes and solvent by using evaporation equipment to increase the concentration of  
said aqueous stream to a selected concentration factor by generating a low solute  
containing distillate stream and retaining at least a portion of said aqueous feed  
5 stream in said evaporation equipment to increase the concentration of a selected  
solute to a selected concentration factor in said retained portion of said aqueous feed  
stream, the improvement which comprises controlling solutes, multi-valent metal  
cations, alkalinity, and carbon dioxide in said aqueous feed stream to a level where

the tendency to form scale is effectively eliminated at said selected concentration  
10 factor, by

(a) prior to feeding of said aqueous feed stream to said evaporation  
equipment, in any order,

(I) minimizing multi-valent cations in said aqueous feed  
stream,

15 (II) minimizing alkalinity of said aqueous feed stream,

(III) minimizing gases dissolved or suspended in said aqueous  
feed stream;

(b) then, after step (a), increasing the pH of said aqueous feed  
stream in said evaporation equipment to at least about 9, or higher.

92. The process as set forth in claim 1, or claim 78, or claim 90, or claim  
91, further comprising, during the step of removing alkalinity, the additional step of  
removing substantially all non-hydroxide alkalinity not associated with hardness.

93. The process as set forth in claim 90, or claim 91, wherein the step of  
raising the pH of said feed water stream, comprises raising the pH to between about  
10 and about 11.

94. The process as set forth in claim 90, or claim 91, wherein the step of  
raising the pH of said feed water stream comprises raising the pH to between about  
11 and about 12.

95. The process as set forth in claim 90, or claim 91, wherein the step of  
raising the pH of said feed water stream comprises raising the pH to between about  
12 and about 13.

96. The process according to claim 1, wherein said feed water stream  
comprises effluents from hydrocarbon recovery operations as produced water.

97. The process as set forth in claim 90, or claim 91, or claim 91, wherein  
during the step of raising the pH of said feed water stream comprises raising the pH  
to between about 9 and about 10.

98. The process as set forth in claim 19, wherein a high solids containing waste stream is generated and, further comprising, de-watering of said high solids containing waste stream.

99. The process as set forth in claim 98, wherein a low suspended solids stream is generated and, further comprising directing said low suspended solids stream back to the inlet of said softener.

100. The process as set forth in claim 90, or claim 91, wherein the step of raising the pH of said feed water stream comprises raising the pH to greater than or at least about 13.

101. The process as set forth in claim 1, wherein the steps of (b) removing multi-valent cations, and (c) removing alkalinity, removing dissolved gases, and increasing pH are accomplished prior to a membrane process to pre-concentrate the feed stream upstream of said heat transfer equipment described under step (d).

102. The process as set forth in claim 1, wherein the removal of multi-valent cations and partially raising the pH are accomplished prior to pre-concentrating said feed stream in a membrane process prior to step (c).

103. Apparatus for treatment of a feed water stream, said feed water stream characterized by the presence of two or more of the following:

(I) multi-valent metal cations,

(II) alkalinity,

(III) at least one molecular species which is at low ionization levels

when in solution at around neutral pH,

to produce a low solute containing distillate stream and a high solute/solids containing blowdown stream, said apparatus comprising:

a) pretreatment equipment for effectively eliminating the

tendency of said feed water to form scale on heat transfer surfaces

when said feed water is concentrated to a desired concentration factor

at a selected pH, comprising, in any order:

(I) at least one softener for removing a portion or

substantially all multi-valent cations from said feed stream,  
and one or more of the following:

(II) at least one de-alkalizer for removing essentially all alkalinity from said feed water stream,

(III) a degasifier for removing dissolved gases,

(IV) chemical addition apparatus for raising the pH of said circulating solution in said heat transfer equipment to a selected pH of at least about 9 by adding a selected base thereto, to urge said at least one molecular species with low ionization levels when in solution at about neutral pH toward increased ionization;

(b) one or more evaporator units, said one or more evaporator units, treating said feed water to produce a high solute/solids containing blowdown stream and a low solute containing distillate stream, and to concentrate said feed water to said selected concentration factor.

104. The apparatus as set forth in claim 103, further comprising, downstream of one or more said evaporator units, to further process said low solute containing distillate stream therefrom, a cation exchange unit.

105. The apparatus as set forth in claim 103, further comprising, downstream of one or more said evaporator units, to further process said low solute containing distillate stream therefrom, an anion exchange unit.

106. The apparatus as set forth in claim 103, further comprising, downstream of one or more said evaporator units, to further process said low solute containing distillate stream therefrom, at least one mixed bed ion exchange unit.

107. The apparatus as set forth in claim 104 or claim 105 or claim 106, further comprising an ion exchange resin regenerator that generates an ion exchange regenerant stream, and further comprising means for directing said ion exchange regenerant stream to the inlet of said degasifier unit in order to treat said ion exchange regenerant stream in said evaporator.

108. The apparatus as set forth in claim 103, further comprising, downstream of one or more said evaporator units, to further process the said low solute containing distillate stream therefrom, a continuous electrodeionization unit to produce (a) a substantially solute free water stream and (b) a solute containing waste stream.

109. The apparatus as set forth in claim 108 further including means for directing said solute containing waste stream to the inlet of said degasifier for further processing.

110. The apparatus as set forth in claim 105, further comprising de-oiling apparatus upstream of said multi-valent cation removal softener.

111. The apparatus as set forth in claim 103, further comprising filtration equipment downstream of said softener.

112. The apparatus as set forth in claim 103, further including means for directing backwash water to the inlet of said softener for further processing.